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Variation of the intermolecular distance with temperature of the mesogen CCH_5

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Abstract : The cyanocyclohexyl cyclohexane CCH_5 ($C_{18}H_{31}N$) shows the following phase transitions :

$$\text{Smectic 1} \xleftarrow[39^\circ C]{} \text{smectic 2} \xleftarrow[50^\circ C]{} \text{nematic} \xrightarrow[62^\circ C]{} \text{Solid} \xrightarrow{85^\circ C} \text{isotropic}$$

X-ray diffraction studies have been conducted on the mesogen in the solid and liquid phases. However, the temperature variation of its parameters namely apparent molecular length/layer thickness/and intermolecular spacing D in the liquid mesophase has not been determined to date. In the present work, X-ray photographs of the sample in the liquid phase has been taken at different temperatures and the variation of intermolecular separation with temperature determined. The results have been compared with X-ray data in the solid phase.

Keywords : Mesogen, thermotropic, X-ray, intermolecular distance.

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1. Introduction

Various properties of the different members of the homologous series of trans - trans-4-alkyl bicyclohexyl-4-carbonitrites (CCH_n) having the structural formula

$$C_nH_{2n+1}$$

have been studied extensively. Electric permittivities and elastic constants have been determined as a function of temperature [1], IR-Raman scattering studies have been conducted on some members by [2] and optical anisotropy and orientational order parameter have been determined as a function of temperature [3,4]. X-Ray diffraction work has been carried out on some members [5,6]. The molecular structure in the solid phase has been determined for the members CCH_3, CCH_5 and CCH_7 by X-ray diffraction [7,8]. However, the determination of intermolecular distance D and apparent molecular length/ layer thickness l in the liquid mesophases have not been studied systematically as a function of temperature. In the present work, X-ray diffraction studies have been conducted on one member, namely CCH_5 at different temperatures to determine the intermolecular distance in the liquid mesophase as a function of temperature.

The compound CCH_5 having the structural formula

$$C_5H_{11}-$$

Molecular formula : $C_{18}H_{31}N$

is known to undergo the following phase transitions (phase transition temperatures supplied by Merck Ltd.)

$$\text{Smectic 1} \xleftarrow[39^\circ C]{} \text{smectic 2} \xleftarrow[50^\circ C]{} \text{nematic} \xrightarrow[62^\circ C]{} \text{Solid} \xrightarrow{85^\circ C} \text{isotropic}$$

From texture studies, it has been suggested [3] that the smectic 2 and smectic 1 phases are the smectic B and smectic G phases respectively.

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2. Experimental methods

Preliminary microscopic studies were conducted using a polarising microscope (Leitz) using a hot stage (Mettler FP82HT) prior to the X-ray diffraction studies to confirm the phase transition temperatures. The transition temperatures as observed were found to be as follows

$$\underset{\text{Smectic 1}}{\overset{39.9^\circ C}{\longleftarrow}}\ \underset{\text{smectic 2}}{\overset{51.0^\circ C}{\longleftarrow}}\ \underset{\text{nematic}}{\overset{85.6^\circ C}{\longleftarrow}}\ \underset{\text{Solid}}{\overset{63.3^\circ C}{\longrightarrow}}\ \underset{\text{nematic}}{\overset{85.6^\circ C}{\longrightarrow}}\ \text{isotropic}$$

A. X-ray diffraction studies

The sample in the form of powder at room temperature was melted and drawn into a thin walled glass capillary of approximately 1 mm diameter. The glass capillary was placed in a hole drilled along the diameter of the cylindrical brass block of the sample holder (designed and fabricated in house), so as to be along a direction perpendicular to the X-ray beam. No filter was used. X-Ray diffraction photographs of the sample were recorded with CuKα radiation on a flat plate Laue camera, exposure time being of the order of 10–12 hours. The temperatures were measured and regulated with the help of a thermocouple inserted in a brass block of the sample holder and connected to a temperature controller, the temperatures being controlled and recorded with an accuracy of ±1°C. Schematic diagram of the experimental arrangement and sample holder are depicted in Figures 1(a) and (b).

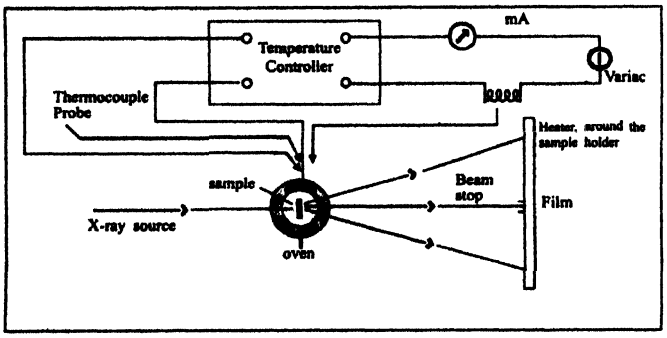

Figure 1(a). Experimental arrangement.

Prior to the X-ray exposure, the sample was taken through a number of temperature cycles reaching a maximum of 90°C (beyond the clearing point), the X-ray diffraction photographs of the sample were taken at different temperatures in the absence of an aligning field while cooling from the isotropic phase. Photographs were taken at 80°C, 70°C, 60°C, 55°C in the nematic phase, at 45°C in the smectic 2 phase and at room temperature (~30°C) in the smectic1 phase.

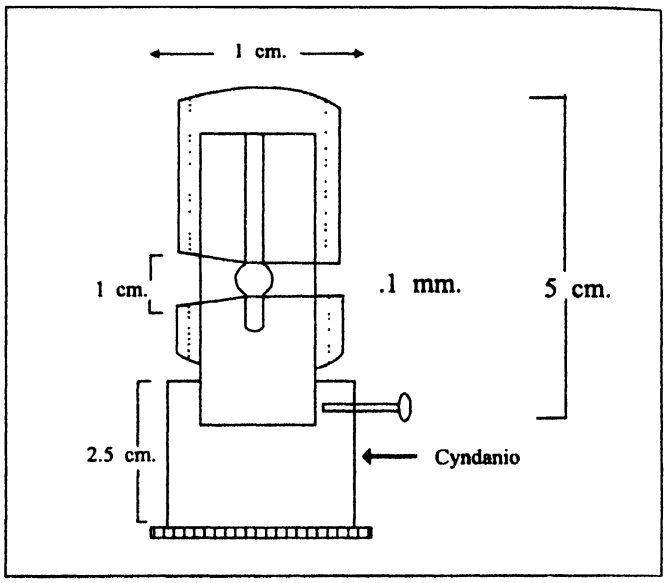

Figure 1(b). Sample holder.

The X-ray photographs were scanned linearly using a HP scanjet 2200c scanner and intensity plot obtained using Image Pro Plus software. The diameters of the rings were obtained from the intensity plot. Sample to film distance was measured accurately by calibrating with (111) reflection of aluminum.

3. Results and discussion

The X-ray photographs taken at some of the temperatures in non-aligned state are depicted in Figure 2. All the photographs (expect the one at room temperature ~30°C) show one ring each, which corresponds to the intermolecular spacing D. The ring/arcs corresponding to the apparent molecular length/layer spacing (usually of much larger magnitude than D and appearing as rings of smaller diameter than that due to D in the reciprocal space in which the photographs are taken) has not appeared in the photographs due to the presence of the beam stop and requisite modification of the experimental arrangement for obtaining the halo corresponding to this inner ring is in progress. D has been calculated using de Vries relation $2D \sin\theta = 1.117\lambda$ as given in [9]. The variation of D with temperature is shown in Figure 3. The photograph taken at the room temperature of 30°C corresponds to the smectic 1 phase and shows the presence of two rings. The presence of the additional ring is evidently due to an additional repeat distance characteristic of the corresponding mesophase. This finding

is in agreement with the phase identification of smectic 1 phase from texture studies conducted [3] where the smcetic 1 phase has been identified as the smectic G phase-which has a two dimensional inplanar arrangement within each layer giving rise to two intermolecular distance parameters. These two D values corresponding to the two group $P2_12_12_1$ [8] compares well with our D value of ~5.1Å.

4. Conclusion

From the nature of the variation of D with t in Figure 3 we would like to conclude that within the nematic phase the intermolecular distance depicts a gradual, continuous

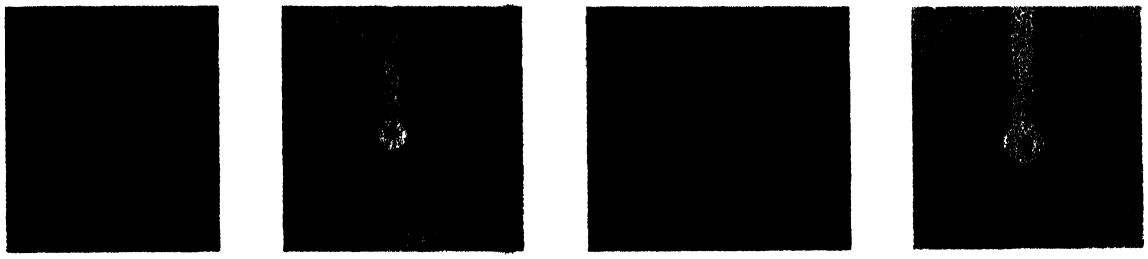

Figure 2. X-ray photograph of CCH_5 (a) at room temperature (b) at 55°C (c) at 70°C (d) at 80°C.

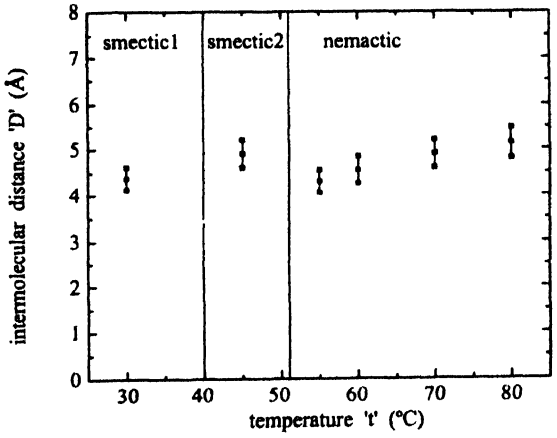

Figure 3. Variation of D with t for CCH_5.

rings have been calculated to be 4.4 Å and 7.6 Å In the smectic 2 phase, the single repeat distance D has a slightly higher value of 5.0 Å. In the nematic phase the D value increases with temperature from 4.6 Å at 60°C to 5.1 Å at 80°C. Though the D values show a continuous gradual increase with temperature in the nematic phase there are discontinuities in the D values as we go from one phase to another. Single crystal diffractometry conducted on single crystals of the sample grown by the present authors (unpublished) under room temperature condition revealed the space group to be $P2_12_12_1$ with cell constants a = 9.483Å, b = 31.296 Å, c = 5.707 Å, R = 0.0630. This is in agreement with the structure obtained in [8]. The sample is also known to crystallize in another form, space group $P2_1/c$ [7]. The lattice constant of a = 5.563 Å when the sample crystallizes in the space group $P2_1/c$ [7] and also the lattice constant of a = 5.707 Å when the sample crystallizes in the space increase with temperature. The increase of D with temperature however is not true in general as we go from one phase to another as is evident in the transition from smectic 2 to the nematic phase where a discontinuity in this parameter exists.

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